



Kinetics of supercritical water oxidation of isopropanol as an auxiliary fuel and co-fuel



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HIGHLIGHTS

- Isopropanol is a suitable fuel for SCWO and is resistant to pyrolysis–hydrolysis.
- Kinetic model of IPA as auxiliary fuel in SCWO start-up stage was proposed.
- Kinetic model of IPA as co-fuel in SCWO under steady-state was proposed.

ARTICLE INFO

Article history:

Received 1 October 2012

Received in revised form 13 March 2013

Accepted 15 March 2013

Available online 4 April 2013

Keywords:

Supercritical water oxidation (SCWO)

Isopropanol (IPA)

Kinetics

Auxiliary fuel

Co-fuel

ABSTRACT

Nowadays the studies that deal with the supercritical water oxidation (SCWO) of problematic wastes are focused in the search of practical solutions for the SCWO main drawbacks: corrosion, plugging, and high running costs. Regarding the high running costs, an important fact is that significant energetic requirement does exist during the process start-up, as well as to reach an autothermal operation if the waste to be treated does not have enough inherent heating value. The use of organic solvents [such as methanol (MeOH), ethanol (EtOH) or isopropanol (IPA)] as auxiliary fuel (to aid running the start-up stage)/co-fuel (to improve the steady-state stage) in the SCWO of certain wastes is emerging as a possible solution to help overcoming these problems. Many works in the literature use IPA as fuel in the SCWO process. However, there are very few laboratory studies that detail, from a practical point of view, the kinetics of the IPA oxidation in supercritical water (SCW) with the aim of unveiling the insights of its behaviour as an auxiliary fuel/co-fuel in the SCWO process and the development of further works on the simulation at a larger scale.

The aim of this work was to develop a detailed and practical set of kinetic equations easily applicable to further studies on simulation and experimentation at a larger scale. In addition, pyrolysis–hydrolysis tests in SCW were also conducted concluding that, in the case of IPA, these reactions do not significantly interfere with SCWO. The required experimentation was performed in a tubular reactor system at laboratory scale at a constant pressure of 25 MPa, using pure oxygen as oxidant and monitoring the efficiency of the oxidation process in terms of reduction in chemical oxygen demand (COD) and total organic carbon (TOC) versus the residence time. This study consists of two major blocks: (a) a set of experiments on SCWO of IPA under a constant excess of oxygen (=100%) and different temperatures ranging from 673 to 773 K. Two-parameter mathematical models involving two steps (a fast reaction followed by a slow reaction) were proposed to describe the IPA SCWO kinetics and to calculate the corresponding kinetic parameters, assuming a zero order for oxygen concentration; and (b) a complementary set of experiments on SCWO of IPA at a constant temperature (748 K) and different oxidant coefficients from $n = 0.5$ (50% of stoichiometric oxygen) to $n = 2.0$ (100% oxygen excess), proposing a kinetic model for oxygen concentration dependence whose parameters were determined using a Runge–Kutta-fourth-order algorithm. The kinetic models proposed allow the prediction of the COD or TOC conversion with or without respect to oxygen supply in order to optimize the SCWO operating conditions and to minimize investment and operating costs.

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1. Introduction

1.1. Generalities on SCWO of wastes

Supercritical Water Oxidation (SCWO) is a high-pressure high-temperature process for the efficient destruction of an extensive diversity of aqueous organic wastes [1] such as textile wastewater, wastewater from terephthalic acids, food waste, municipal excess sludge, manure sludge, oily wastes, alcohol distillery wastewater, obsolete chemical weapons, wastes from nuclear industry or pharmaceutical and biopharmaceutical wastes [2,3]. SCWO is based on the oxidation in aqueous medium under conditions over the critical point of pure water, usually in the range [673,923] K and commonly at a pressure around 25 MPa. Under these conditions, water exhibits unique physical–chemical properties that make it an effective medium for oxidation, where organics and oxygen form a homogeneous phase. Thus, mass transport limitations are minimized leading to high reaction rates and conversions close to unity in short residence times and small reactor volumes. Moreover, as the oxidation reactions are exothermic, autothermal operation and even heat production could be achieved in the SCWO process [4–7].

As an example of the latest trends in this field, the implementation of the SCWO process as tertiary treatment in the sludge line of wastewater treatment plants (WWTPs) is increasingly regarded as an alternative to incineration [8–10], in order to promote the removal of the excess sewage sludge [3,10–14]. The studies focused on the improvement of sewage sludge SCWO performance, effectiveness and reliability are quite numerous [3,15]. In fact, the main drawbacks that keep SCWO away from being massively implemented on a full-scale at WWTPs and other industries are corrosion, plugging and high running costs [3]. In particular, severe operating conditions (high temperature, high pressure, high concentration of oxidant and extreme pH value) together with high concentration of ionic species, free radicals, acids and inorganic salts result in severe corrosion problems in the SCWO reactor and the inlet/outlet pipelines.

To help overcoming these limitations, accomplish an autothermal operation and, in general, a better performance of the SCWO process, methanol (MeOH), ethanol (EtOH) or isopropanol (IPA) can be added as auxiliary fuels during the start-up or as co-fuels during the steady-state of the SCWO process for certain wastes. Some major candidates among the wastes that may require the use of a fuel are obsolete chemical weapons, biomass slurries, sewage sludge, manure sludge or, in general, wastes with low inherent heating value, high acute toxicity and/or high concentration of ammonia [16,17].

1.2. Auxiliary fuels for SCWO

It is well known that the energy consumption to heat the waste externally during the SCWO process may become prohibitive upon scale-up from a laboratory system [3]. In addition, an excessive preheating during the process start-up to initiate rapid reaction effectively, limits the concentration of waste that can be processed due to char formation and plugging [18] in the preheating pipeline, mainly in the case of high salt-containing wastes. Furthermore, in the case of wastes containing solids (e.g., biomass slurries) it is necessary to work at high flow rates to avoid solids deposition, so the start-up of the process would require too much energy. In this way, it is better to start-up the process at a low flow rate and, afterwards, to increase the flow rate gradually. This is why the use of an auxiliary fuel to carry out the SCWO start-up becomes mandatory, allowing the heating process to start at a low flow rate, and once the required temperature is attained, to proceed to grad-

ually increase the system flow rate. Then, after the steady-state is reached (under the desired operating conditions), it is time to proceed with the injection of the waste.

As a result, the use of an auxiliary fuel such as IPA [that is easily oxidized by SCWO and presents a higher heat of reaction ($\Delta H_r = -1908$ kJ/mol) than MeOH ($\Delta H_r = -650$ kJ/mol) and EtOH ($\Delta H_r = -1279$ kJ/mol)]* to conduct the start-up of the SCWO process, induces a proper operation in this early stage and greatly facilitates reaching the subsequent steady-state stage efficiently. The employment of IPA to start-up the SCWO process is intended to maximize the heat of reaction generation, in order to minimize the time to reach the suitable operating conditions (autothermal operation) before the considered waste is injected and subjected to SCWO under steady-state. During the SCWO start-up performed using an organic solvent, it is also favourable not to restrict the addition of oxidant (air or oxygen in excess) to aid the maximization of the heat of reaction generation and the minimization of the start-up operating time. Besides, this does not entail an excessive increase of the overall operation costs, as it only constitutes a punctual overspending during the start-up of the process that, moreover, is offset enough and to be spared by the patent reduction in the start-up operation time. (*Heat of reaction values estimated at 673 K and 25 MPa according with the empirical equation proposed by Cocero et al. [4]).

The application of a two-step first order kinetic model to the SCWO process assumes that the SCWO reaction occurs in two well differentiated phases: (1) a fast initial reaction in which easy oxidizable molecules are decomposed at a high rate to CO_2 , H_2O and a mixture of intermediate products of a more refractory nature, followed by (2) a slow subsequent reaction where the main part of those intermediates formed before and other refractory molecules initially present in the wastewater/waste, are progressively decomposed to more simple molecules (alcohols, organic acids, etc.) and mineralized down to CO_2 , H_2O , N_2 , and salts. It is important to point out that depending on the operation temperature, there are some refractory intermediates (such as acetic acid and ammonia) that may remain in the effluent even at the higher residence times studied. This type of kinetic model was satisfactorily applied in our previous works dealing with the oxidation of cutting fluids in SCW on laboratory scale [19] and pilot plant scale [20]. Two-step first-order kinetics has also been proposed previously in the literature for other feeds such as wastewater from the textile industry, oxalic acid and acrylic acid [21,22].

This work, which aims to describe the kinetics of the SCWO process start-up using IPA, proposes and develops a two-step first-order kinetic model according to the results obtained from SCWO of IPA experiments at constant pressure and oxidant excess conditions, and under different temperatures and residence times. The corresponding section of this work (Section 3.2) includes two kinetic models of this nature, each of them based on the chemical oxygen demand (COD) removal and total organic carbon (TOC) removal results, respectively. This approach will be useful for further works on IPA as auxiliary fuel in the start-up stage of the SCWO process on larger scales, in order to aid running this stage while minimizing the required external preheating electrical power.

1.3. Co-fuels for SCWO

After reaching the proper steady-state conditions for the SCWO of certain waste, the oxidant consumption becomes an important factor to consider in the economic balance of the process [15]. Therefore, the oxidant coefficient must be optimized to minimize running costs without impairing the organic matter removal during the SCWO process. Besides, the addition of moderate doses of an organic solvent (e.g. IPA) as co-fuel in the SCWO of wastes under steady-state conditions facilitates the maintenance of an

autothermal operation, optimizing the oxidant consumption and, therefore, relieving the just mentioned main drawbacks of this technology: corrosion, plugging and high running costs.

Furthermore, another benefit of employing organic solvents as co-fuels is the patent enhancement of the ammonium (NH_4^+) removal during the SCWO process of wastes, such as anaerobically digested sewage sludge with a high concentration of nitrogenous compounds and ammonium, which are difficult to eliminate by SCWO and are so harmful to the environment. Works that deal with the use of organic solvents during SCWO to improve the reliability of the process while enhancing, in general, the removal of organic matter and, in particular, the removal of ammonium can be found in the literature [8,23,24]. As a summary of them, the addition of hydrocarbons easily oxidized by SCWO aided the achievement of an ammonia removal improvement, even operating under lower temperatures. Moreover, the experience of Killilea et al. [25] in SCWO must be highlighted, as it states that the key in order to achieve a complete oxidation of nitrogen species to N_2 (over the conversion to nitrous oxide (N_2O)) and to avoid the accumulation of nitrate (NO_3^-) and nitrite (NO_2^-) in the liquid effluent (which favours corrosion of the SCWO reactor [26]), is to add a hydrocarbon/organic solvent, decrease the oxidant excess, and increase the temperature during the SCWO process. Results from Bermejo et al. [27] are particularly encouraging since, as they claimed, the oxidation rate of NH_3 obtained in their reactor is higher than the fastest kinetic data found in the literature, being the presence of IPA or its associated radicals and transient oxidation products (e.g. H_2O_2 according to Croiset and Rice [28]) one of the main reasons to explain the considerable enhancement of the SCWO process. Besides, considering global warming and general environmental aspects, the minimization of nitrogen species in the liquid effluent along with the abatement of N_2O gaseous emissions [29] from SCWO process operated under the mildest possible conditions would be a definite lever to help this process become a real and environmentally friendly alternative for waste management at a global scale.

In this work, to describe the kinetics of SCWO of IPA considered as co-fuel, a kinetic model for oxygen concentration dependence has been proposed and developed in accordance with the results from experiments on the IPA SCWO at constant pressure and under different oxidant coefficients, temperatures and residence times. The corresponding section of this work (Section 3.3) deals with the determination of kinetic parameters, using a Runge–Kutta algorithm and employing the obtained COD removal results. This approach will be useful for further experimental, design and scaling works on IPA as co-fuel in the SCWO process at a larger scale (mainly in the steady-state stage).

From the point of view of economic costs and environmental aspects, caution must be exercised with the use of organic solvents as auxiliary fuel/co-fuel in the SCWO process. In fact, a system design that avoids the use of external heat exchangers is a not so much beneficial alternative for the energetic and economical balances of the SCWO process [30]. That mentioned design excludes the external heat exchangers in order to decrease the investment costs and prevent the solid precipitation, corrosion and plugging that may occur in that equipment, therefore proposing only the mixing of the feed, the oxidant and the co-fuel. Hunter et al. [31] support the accomplishment and maintenance of an autothermal operation with the aid of IPA avoiding external heating. Even so, the dose of organic solvent must be optimum and must also be accompanied by optimum operating conditions. That is another reason to minutely describe the behaviour and kinetics of those additives in SCWO, in order to aid the optimization of its application. Some works in the literature even defend the use of other wastes such as trap grease, plastics or rubber instead of organic solvents as auxiliary fuel/co-fuel [32,33]. However, the use of that type of

wastes as fuel in SCWO may provoke problems related with pyrolysis in the preheaters and accumulation of ammonia. But it is known that, compared to other solvents, IPA is considered relatively non-toxic and it is widely used as dry cleaning solvent in several fields of the industry such as semiconductor manufacturing [34,35]. In fact, a 63 kg/h full-scale SCWO facility was built for the Nittetsu Semiconductor factory for the elimination of semiconductor manufacturing wastes [36,37]. Therefore, it may be useful to know in depth the behaviour and kinetics of IPA during SCWO not only from the point of view of IPA itself being used as auxiliary fuel/co-fuel, but also from the point of view of IPA being one of the major constituent of the semiconductor manufacturing cleaning waste, which could be suitable for being reused as auxiliary fuel/co-fuel in SCWO of, for example, sewage sludge. In that case, the process will receive revenue to accept this negative value abundant waste as complementary feed and even better if the semiconductor manufacturing factory is near a WWTP provided with a SCWO unit.

1.4. SCWO of organic solvents: kinetics

To this date, there is a number of works in the literature that deal with the kinetic study of organic solvents (such as MeOH, EtOH and IPA) oxidation in SCW. According to all of them, first-order kinetic models satisfactorily describe the involved reactions. The most common studies of this nature are those focused in the SCWO of MeOH [38–45], followed by those dedicated to SCWO of EtOH [45–47]. However, only one work deals with the kinetics of IPA oxidation in SCW [31] and another one alludes to complementary aspects of the former [46] comparing oxidation kinetics of MeOH, EtOH, 1-propanol and IPA in SCW. (By contrast, works related with the dehydration of IPA in SCW and associated kinetics are quite common in the literature [48–50]). Hunter et al. [31] proposed first-order kinetics for the destruction of IPA by means of SCWO. In that work, acetone was found to be the main intermediate in the SCWO of IPA and, assuming that the production rate of acetone was equivalent to the destruction rate of IPA, first-order kinetics for the destruction of acetone was also proposed. That proposal was based on empirical data from SCWO experiments lasting from 0.5 to 2.4 s under temperatures ranging from 673 to 753 K at constant pressure and oxygen excess around 24.5 MPa and 15%, respectively. It is to be highlighted that all those works are not focused on the removal of the COD and TOC generated from the oxidation of the organic solvent in study, but on the conversion of the organic solvent itself. Other works such as Krajnc and Levec [51] studied the SCWO of IPA in a tubular reactor through a few experiments lasting from 15 s to 30 s at approximately 658 K, 23.3 MPa and 135% excess of oxygen, presenting the efficiency of the process in terms of TOC removal, but no kinetic equations were proposed. The previously cited work by Cabeza et al. [24] also presented TOC removal results for a few preliminary SCWO experiments with IPA in a tubular reactor at around 673 K, 23 MPa and from 38% to 145% oxygen excess, but again with no reaction kinetics proposed. In fact, in order to perform the simulation of the SCWO of IPA, Bermejo et al. [27,52,53] used the general kinetics pathways reported by Li et al. [54] (for the wet oxidation (WO) of organic compounds) and used kinetics parameters given by works that developed kinetic models validated for the SCWO of phenol, n-octanol and acetic acid [55,56].

Therefore, a work dealing with an exhaustive kinetic study on the SCWO of IPA was necessary but was not available in the literature yet. This work is based on the measurement of total conversions in terms of the removal of global parameters such as COD and TOC, presenting experimental results for a wide range of temperatures (from 673 to 773 K) and residence times (from 4 to 80 s) and also considering the IPA SCWO process kinetics dependence on the oxygen concentration, with the aim of learning more about the

behaviour of IPA in the SCWO process from a practical point of view. As a summary of what is going to be shown in this work, according to these results two different types of kinetic models have been proposed and developed for the SCWO of IPA considered, on the one hand, as auxiliary fuel (to aid running the start-up stage) and, on the other hand, as co-fuel (to improve the steady state stage).

2. Materials and methods

2.1. Reactants

Isopropanol (C_3H_8O , Panreac, 99% purity) was used as feedstock in this work. Hydrogen peroxide (H_2O_2 , Panreac, 33% w/v aqueous solution) was used as source of oxygen. Diluted feed solutions of the required concentration were made *in situ* by using distilled and deionized water.

2.2. System and procedure

The SCWO experiments of this work were conducted in a typical continuous flow tubular system. A schematic diagram of the system can be consulted in our previous publications [19,57]. The tubular reactor was built from 1/4 in. diameter AISI 316L SS tubing. In the present work, a set of experiments was conducted with a reactor volume of 80.94 cm^3 while for another set, to allow the study of shorter residence times, 2.42 m were cut from the reactor and removed from the system resulting in a reactor volume of 39.94 cm^3 . The system includes an oxidant tank and a feed tank where the correspondent H_2O_2 and IPA solutions were loaded, respectively. The IPA solution was continuously stirred during the experiments. Both oxidant and feed streams were firstly pressurized and then preheated throughout two independent lines by means of two high-pressure metering pumps (MILTON ROY) and spiral heating resistances, respectively. Two in series preheaters were used for the oxidant stream achieving a complete decomposition of H_2O_2 to H_2O and O_2 , as reported also by Krajnc and Levec [51] and Croiset et al. [58]. After preheating until approximately 473 K, the two lines converge into one at the reactor entrance where both streams get mixed, with the tubing being within a fluidised sand bath (TECHNE SBL-2D) in order to enable an isothermal reaction. An air blower allowed the homogenization of the medium in the sand bath. The reaction temperature was monitored by means of thermocouples installed at the reactor's inlet and outlet. Upon exiting the reactor, the effluent was quenched in a counter-current heat exchanger and afterwards, the system pressure was reduced to atmospheric by means of a backpressure regulator. Then, liquid and vapour phases of the product stream were separated, being able to collect liquid samples and to conduct gas composition analysis by direct connection with the gas chromatograph. The gas flow rate was monitored by means of a bubble flow meter.

At the beginning of each experiment, before pumping the H_2O_2 and IPA solutions, the system was started-up pumping distilled and deionized water throughout both lines. The fluidised sand bath was then heated up to the desired temperature. Once the pumps flow rates, reactor pressure and temperature were stabilized, the pumping of water was switched to pumping of H_2O_2 and IPA solutions. Afterwards, the system took approximately 15 min to get stabilized again. Flow rates for the oxidant and organic feed streams ranged from 4.2 ml/min to 15.8 ml/min and from 2.8 ml/min to 57.7 ml/min, respectively. The flow rates were monitored by means of the absolute method. Pressure was fixed at 25 MPa. Temperatures ranged from 673 to 773 K. Reactor residence times were calculated from water density at experimental

conditions, reactor volume, and total feed flow rate. The initial concentration of IPA at the reactor entrance was $3948 \pm 334\text{ (mgIPA l}^{-1}\text{)}$, which corresponded to $[COD]_0 = 9460 \pm 800\text{ (mgO}_2\text{ l}^{-1}\text{)}$ and $[TOC]_0 = 2696 \pm 250\text{ (mgC l}^{-1}\text{)}$. More specific details of the experimental apparatus and procedure are described in our previous studies [19,57].

2.3. Sample analysis

COD and TOC concentrations of liquid samples were monitored. All the analyses were performed according to 'Standard Methods for the Examination of Water and Wastewater' [59]. COD analysis was conducted by closed reflux colorimetric method (5220D). The combustion-infrared method (5310B) was conducted in a TOC analyzer SHIMADZU 5050. The composition of final gaseous effluent (H_2 , CO_2 , O_2 , N_2 , CH_4 and CO) was analyzed using a HP 6890 PLUS gas chromatograph with a thermal conductivity detector (TCD). Two columns coupled in series were used to separate CO from CO_2 : the first column was a Porapak-Q column and the second was a molecular sieve Carbosieve column (SUPELCO). The monitoring of the gaseous effluent (flow rate and composition) helped checking out the correct operation of the system and that no unwanted reactions occurred.

3. Results and discussion

3.1. Pyrolysis–hydrolysis of IPA in supercritical water

References on pyrolysis–hydrolysis of organic solvents such as MeOH [60], EtOH [61,62] and IPA [63,64] can be found in the literature. Nevertheless, as far as authors are concerned, only a few studies have recently been carried out on the pyrolysis–hydrolysis in SCW of these organic solvents (MeOH: [42]; EtOH: [65]), being especially rare those devoted to IPA [31]. Table 1 summarises the IPA pyrolysis experiments performed in the continuous flow reactor system employed in this work. All of them were carried out in the same tubular reactor system used for the SCWO experiments, under a constant pressure of 25 MPa. Experiments were conducted under total absence of oxygen using deoxygenated water to prepare the IPA feed solutions.

For all the experiments in this study, organics removal results from pyrolysis–hydrolysis were one order of magnitude below those obtained in SCWO experiments for comparable conditions. Even under the most severe conditions (Expt. 3) the organics removal by the pyrolysis–hydrolysis of IPA in the preheaters and the reactor was <10%. Therefore, it was not necessary to correct oxidation data for pyrolysis–hydrolysis, especially because most of the oxidation tests were carried out at temperatures below 773 K. A similar deduction can be found in [38,42] for the case of SCWO and pyrolysis of MeOH.

3.2. Kinetics of SCWO of IPA as auxiliary fuel

This stage of the work consisted on conducting a set of experiments of IPA SCWO under different temperatures ranging from

Table 1

Summary of IPA pyrolysis experiments and obtained results in terms of organics removal. Experiments were conducted at 25 MPa.

Expt. no.	Temperature (K)	Residence time (s)	Deoxygenated water	COD removal (%)	TOC removal (%)
1	733	25.66	Yes	2.68	2.45
2	753	24.05	Yes	3.35	3.09
3	773	37.60	Yes	6.68	5.17

673 K to 773 K, a constant pressure of 25 MPa and an oxidant coefficient $n = \text{oxygen}_{\text{supplied}}/\text{oxygen}_{\text{stoichiometric}} = 2.0$ (i.e., an oxygen excess = 100%). The oxygen excess was calculated over the theoretical amount of oxygen required for complete oxidation (that is the stoichiometric amount), taking into account that, a priori, the initial COD concentration of the IPA feedstock solution at the reactor entrance was intended to be around 10 g/l. The efficiency of the process was monitored in terms of both COD and TOC removal.

Results from this set of experiments can be consulted in Table 2. Both the influence of temperature and time was studied. There is a notable proportional relation between those two factors and the COD and TOC removal in the SCWO of IPA. In fact, according to the results shown in Table 2, it can be stated that oxidation of IPA in SCW is significantly successful, since COD and TOC removals of around 94% were registered at 723 K along with a residence time of less than 1 min. Moreover, the experiment conducted under the most severe operating conditions of this work (773 K, 50 s, 25 MPa and $n = 2.0$) yielded COD and TOC removal >99%.

COD and TOC are standardized and global parameters that turn out to be very useful and easily manageable from both an environmental and scaling-up design point of view. Firstly, using the COD concentration and taking into account that under supercritical conditions only one homogeneous phase does exist, and that the oxygen supply was maintained in excess during the experiments ($\beta = 0$), it is possible to model the experimental data according to first-order kinetics as follows:

$$\alpha = 1$$

$$\beta = 0$$

$$\gamma = 0$$

$$r_{\text{COD}} = -\frac{d[\text{COD}]}{d\tau} = k \cdot [\text{COD}]^\alpha \cdot [\text{O}_2]^\beta \cdot [\text{H}_2\text{O}]^\gamma \xrightarrow{\gamma=0} -\frac{d[\text{COD}]}{d\tau} = k \cdot [\text{COD}] \quad (1)$$

where $[\text{COD}]$ is the total chemical oxygen demand (mol l^{-1}), τ is the residence time (s), k is the specific reaction rate constant (s^{-1}) and α is the reaction order for organic compounds that can be assumed as

Table 2

Summary of IPA supercritical water oxidation experiments under different temperatures and residence times, and obtained results in terms of organics removal. Experiments were performed at 25 MPa, 100% oxygen excess (i.e., $n = \text{oxygen}_{\text{supplied}}/\text{oxygen}_{\text{stoichiometric}} = 2.0$), $[\text{COD}]_0 = 9570 \pm 904$ ($\text{mgO}_2 \text{ l}^{-1}$) and $[\text{TOC}]_0 = 2758 \pm 290$ (mgC l^{-1}).

Expt. no.	Temperature (K)	Residence time (s)	COD removal (%)	TOC removal (%)
4	673	11.01	36.24	31.67
5	673	15.01	50.32	46.84
6	673	31.88	57.55	50.26
7	673	65.30	66.74	61.86
8	698	6.18	44.94	40.25
9	698	8.36	50.78	47.77
10	698	10.65	64.17	58.21
11	698	24.18	77.30	73.35
12	698	36.23	81.39	78.37
13	698	84.78	89.80	88.39
14	723	4.91	74.42	71.05
15	723	9.13	82.22	78.77
16	723	19.60	87.22	85.43
17	723	39.10	92.47	91.11
18	723	55.06	93.81	93.27
19	748	4.89	91.42	90.67
20	748	8.59	92.73	91.58
21	748	17.94	97.47	97.08
22	748	33.61	98.43	98.91
23	748	48.74	98.51	98.99
24	773	4.44	98.51	98.34
25	773	8.08	99.67	99.70
26	773	16.12	99.70	99.70
27	773	29.84	99.85	99.89
28	773	40.86	99.88	99.92

equal to unity in the hydrothermal oxidation reaction ($\alpha = 1$) as stated by Dutournié et al. [66]. In a reaction medium containing more than 90% water, the reaction order for water can be neglected, that is, $\gamma = 0$. The COD concentration was used instead of the organic molecule concentration to describe the global kinetics of the organic compound transformation into CO_2 and H_2O [67].

Integration of Eq. (1) yields the following equation:

$$-\ln \frac{[\text{COD}]}{[\text{COD}]_0} = k \cdot t \quad (2)$$

where the COD concentration of the influent ($[\text{COD}]_0$) and the COD concentration of the liquid effluent ($[\text{COD}]$) are put into relation. Eq. (2) allows calculating the different values of k for each temperature according to the experimental results obtained from the SCWO tests (Table 2) and represented in Fig. 1a. An analogous data analysis was performed using the total organic carbon concentration ($[\text{TOC}]$) instead of $[\text{COD}]$ (Fig. 1b). Fig. 1 clearly shows that the evolution of the COD removal and TOC removal regarding time presents two well-distinguished stages: a first step which entails a fast removal of the easily oxidizable compounds and a second step during which the most refractory compounds are slowly oxidized into final products. Talking about the oxidation in SCW of a pure compound like IPA and according to the experience of Hunter et al. [31], it can be considered on the one hand that the compounds which are easily and rapidly oxidized during the first step are mainly IPA itself, acetone (the main intermediate formed and subsequently destroyed during the SCWO of IPA) and other products of IPA partial oxidation; on the other hand, the compounds relatively slowly oxidized during the second step may mainly be acetic acid, acetaldehyde and formaldehyde [47,54].

Therefore, two-step first-order kinetics is proposed in this work for the oxidation of IPA in SCW under conditions of oxygen excess. Through the linear regressions, developed in Fig. 1, of the experimental data corresponding to each temperature and step, the values of the respective specific reaction rate constants (k [s^{-1}]) were estimated and they can be consulted in Table 3.

It is standard practice to express the temperature dependence of k using the Arrhenius equation, as follows:

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (3)$$

where A is the pre-exponential factor (s^{-1} /also called frequency factor for first order kinetics), E_a the apparent activation energy (J mol^{-1}), R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). The logarithmic form of Eq. (3) is the following:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (4)$$

Eq. (4) is represented as $\ln k$ versus $1/T$ plot in Fig. 2 and allows calculating the pre-exponential factor (A) and the apparent activation energy (E_a) for both steps of the proposed kinetics (in this case, with a 95% confidence level).

Finally, the two-step first-order kinetic equations based on both the COD and TOC removal are presented in Table 4.

As it can be seen in Fig. 3, the experimental data and kinetic models predictions match quite properly.

The typical induction time (during which the conversion of the organic solvents is negligible as shown in [24,44]) was not observed in this work (as it happened to Anitescu et al. [42] for the oxidation of MeOH in SCW). The access to results influenced by induction time is facilitated when the experimentation is conducted under low initial concentrations and low temperature or under very short residence times [44]. Operating under residence times below 4 s, other authors have accessed to induction times (of less than 1 s) for the oxidation of IPA in SCW [31], presenting S-shaped conversion-versus-time curves (from 0 to 2.5 s). In the

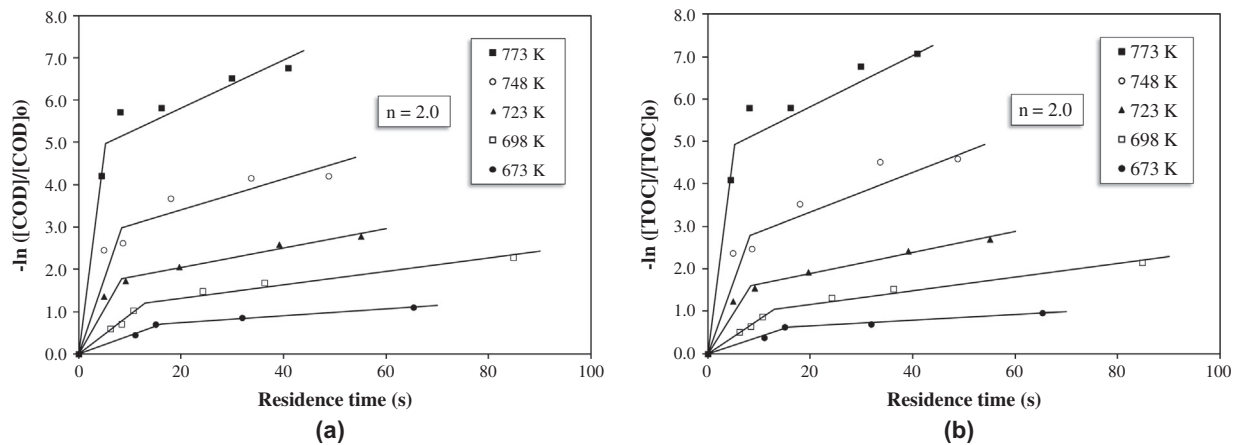


Fig. 1. Kinetic plot for SCWO of IPA at 25 MPa and 100% oxygen excess, considering: (a) chemical oxygen demand concentration ([COD]), with $[COD]_0 = 9570 \pm 904$ ($\text{mgO}_2 \cdot \text{l}^{-1}$); and (b) total organic carbon concentration ([TOC]), with $[TOC]_0 = 2758 \pm 290$ ($\text{mgC} \cdot \text{l}^{-1}$).

Table 3

Specific reaction rate constant values [k (s^{-1})] for the oxidation of IPA in SCW under conditions of 100% oxygen excess and 25 MPa (corresponding to the development of two-step first order kinetic models based on COD and TOC data, respectively).

Temperature (K)	COD		TOC	
	First step (fast) k (s^{-1})	Second step (slow) k (s^{-1})	First step (fast) k (s^{-1})	Second step (slow) k (s^{-1})
673	0.0446 ± 0.0019	0.0079 ± 0.0005	0.0395 ± 0.0025	0.0068 ± 0.0010
698	0.0928 ± 0.0031	0.0157 ± 0.0027	0.0808 ± 0.0013	0.0161 ± 0.0026
723	0.2090 ± 0.0261	0.0233 ± 0.0028	0.1882 ± 0.0244	0.0248 ± 0.0023
748	0.3533 ± 0.0599	0.0364 ± 0.0143	0.3362 ± 0.0598	0.0522 ± 0.0151
773	0.9474 ± 0.0000	0.0567 ± 0.0187	0.9225 ± 0.0000	0.0674 ± 0.0205

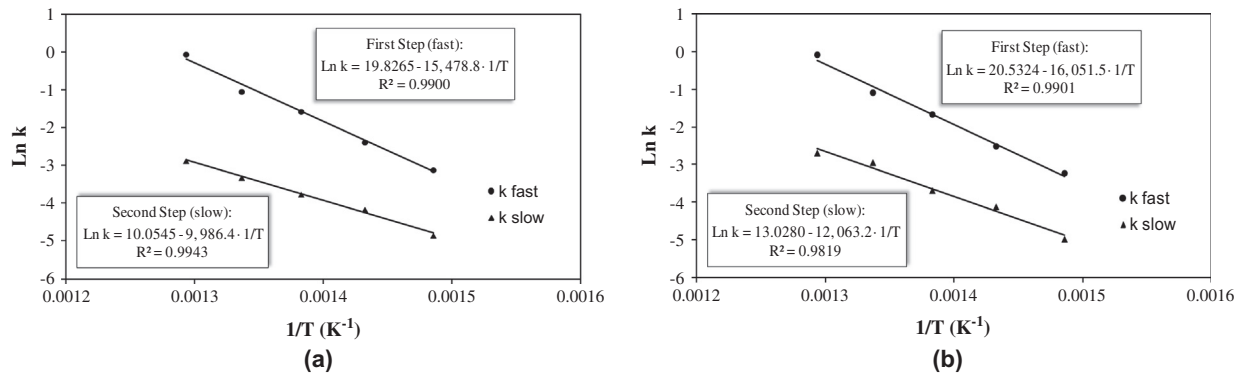


Fig. 2. Effect of temperature on specific reaction rate constants (k) for SCWO of IPA (25 MPa and 100% oxygen excess) based on: (a) COD data and (b) TOC data.

present work the studied residence times were not below 4 s, however, from a practical point of view a kinetic study using higher residence times (equal and over 4 s) is quite appropriate to simulate the post-induction period.

In fact and overall, the kinetic equations presented in Table 4 are quite useful for further studies on the simulation and scale-up of the start-up stage of the SCWO of suitable wastes (such as sewage sludge), using IPA as an auxiliary fuel, to trigger this stage and the achievement of the maximum reaction enthalpy under conditions of oxygen excess and thus, the optimization of the reaction time and the minimization of the start-up operation costs. Simplicity and validity of the proposed models, based on the measurement of total conversions in terms of removal of global parameters such as COD and TOC, allow them to have a practical character and an easier applicability.

3.3. Kinetics of SCWO of IPA as co-fuel

The continued addition of IPA as co-fuel in the steady state of the SCWO process to improve its performance at industrial scale must be based upon previous studies that optimize the oxygen consumption and minimize investment and operating costs. A kinetic model that allows the conversion prediction regarding oxygen supply is quite useful in this sense. As claimed by Vogel et al. [44] in the case of MeOH oxidation in SCW, few authors have developed kinetic models for oxygen concentration dependence assuming this dependence is zero. In fact, as far as authors are concerned, in the case of the oxidation of IPA in SCW, there is no study in the literature presenting an exhaustive kinetic analysis including the oxygen concentration dependence. As Sánchez-Oneto et al. [68] claimed, from an industrial scale point of view it

Table 4
Kinetic equations proposed for the oxidation of IPA in SCW under conditions of 100% oxygen excess and 25 MPa. (Kinetic parameters estimated with a 95% confidence level).

Global parameter	First step (fast)	Second step (slow)	Equation no.
COD	$r_{\text{COD}} = -\frac{d[\text{COD}]}{dt} = (407.8 \pm 81.5) \times 10^6 \cdot \exp\left[-\frac{(128.6 \pm 23.7) \times 10^3}{RT}\right] \cdot [\text{COD}]$	$r_{\text{COD}} = -\frac{d[\text{COD}]}{dt} = (232.6 \pm 44.7) \times 10^2 \cdot \exp\left[-\frac{(83.0 \pm 11.6) \times 10^3}{RT}\right] \cdot [\text{COD}]$	(5) and (6)
TOC	$r_{\text{TOC}} = -\frac{d[\text{TOC}]}{dt} = (826.2 \pm 165.0) \times 10^6 \cdot \exp\left[-\frac{(133.5 \pm 24.6) \times 10^3}{RT}\right] \cdot [\text{TOC}]$	$r_{\text{TOC}} = -\frac{d[\text{TOC}]}{dt} = (455.0 \pm 145.8) \times 10^3 \cdot \exp\left[-\frac{(100.3 \pm 25.0) \times 10^3}{RT}\right] \cdot [\text{TOC}]$	(7) and (8)

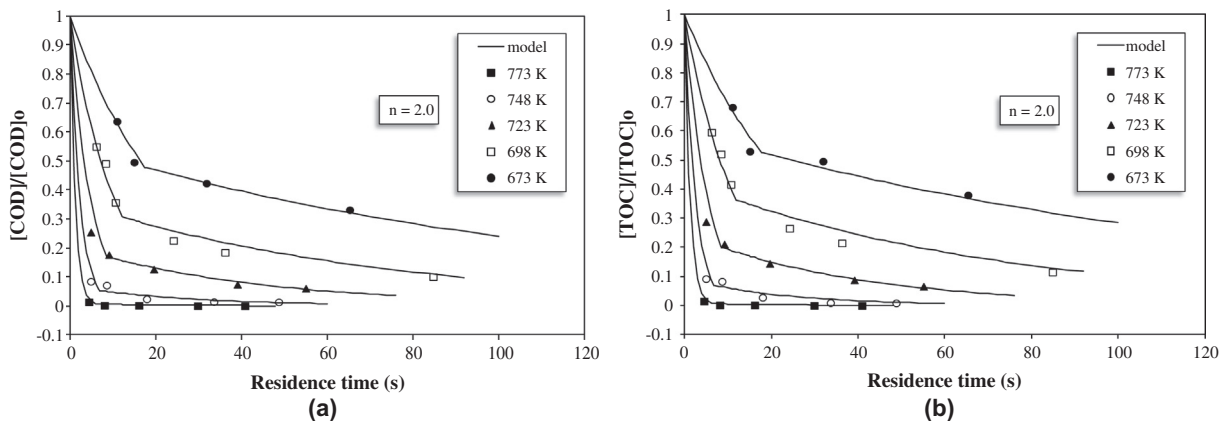


Fig. 3. Two-step first-order kinetic model for the oxidation of IPA in SCW (25 MPa and 100% oxygen excess): predicted profiles versus experimental data expressed as (a) $[\text{COD}]/[\text{COD}]_0$ and (b) $[\text{TOC}]/[\text{TOC}]_0$. Note that $[\text{COD}]_0 = 9176 \pm 582 \text{ (mgO}_2 \text{ l}^{-1})$ and $[\text{TOC}]_0 = 2624 \pm 138 \text{ (mgC l}^{-1})$.

is necessary to optimize the operating conditions needed to obtain a high depurative degree while minimizing investment and operating costs, thus the optimization of oxygen consumption is essential.

Therefore, in order to be able to develop a kinetic model for oxygen concentration dependence, the following stage of this work consisted in performing another set of SCWO experiments of IPA under different oxidant coefficients ranging from $n = 0.5$ to $n = 2.0$, a constant pressure of 25 MPa and a temperature of 748 K, complementing the set already presented in Table 2 of the previous Section 3.2. The initial concentration of IPA at the reactor entrance was $3830 \pm 243 \text{ (mgIPA} \cdot \text{l}^{-1})$, and the efficiency of the process was monitored in terms of COD removal. It is to be highlighted that the equations presented in the previous section are not suitable to model the results from these experiments, since in this case the supplied oxygen is not strictly in excess and thus, it is not possible to assume a zero order for the oxygen concentration.

The results from this complementary set of experiments can be consulted in Table 5. The influence of the oxidant coefficient and residence time is patent. As it was expected, the organic matter removal rate is enhanced with increasing oxidant coefficient. However, it is clear that oxygen dependence is more patent below the stoichiometric value for oxygen concentration than above it. In fact, few differences occurred between the experimental data obtained for tests with $n = 1.35$ and $n = 2.00$ at the highest studied residence times $[\approx(40, 50) \text{ s}]$, 748 K and 25 MPa (similar to what was stated in Cocero et al. [69,70] for residence times of $\approx[40, 90] \text{ s}$). Therefore, it can be a priori stated that for residence times $\geq 40 \text{ s}$ raising n up to values around 2 or higher is not necessary to achieve significant conversion rates. Overall and according to the results shown in Table 5, it can also be stated that it is suitable and necessary to establish a kinetic analysis including the oxygen concentration dependence (a fortiori, assuming that a study of this nature has never been included in the IPA SCWO literature before).

Table 5

Summary of IPA supercritical water oxidation experiments under different oxidant coefficients and residence times, and obtained results in terms of organics removal. Experiments were carried out at 748 K, 25 MPa, $[\text{COD}]_0 = 9176 \pm 582 \text{ (mgO}_2 \text{ l}^{-1})$ and $[\text{TOC}]_0 = 2624 \pm 138 \text{ (mgC l}^{-1})$.

Expt. no.	Oxidant coefficient (n)	Residence time (s)	COD removal (%)
29	0.50	4.81	55.18
30	0.50	11.19	59.47
31	0.85	4.87	63.48
32	0.85	11.46	73.09
33	0.85	25.42	74.99
34	0.85	41.08	75.92
35	1.00	4.75	76.34
36	1.00	12.00	83.70
37	1.00	23.31	87.02
38	1.00	40.45	89.48
39	1.35	4.79	78.13
40	1.35	12.16	85.10
41	1.35	26.25	93.70
42	1.35	41.40	94.35
19	2.00	4.89	91.42
20	2.00	8.59	92.73
21	2.00	17.94	97.47
22	2.00	33.61	98.43
23	2.00	48.74	98.51

All the experiments included in Tables 2 and 5 have been used to develop a kinetic model based on the oxygen concentration dependence for the SCWO of IPA. This model complements the kinetics presented previously in this work and those presented in Hunter et al. [31], where the oxygen concentration dependence was not taken into account.

Mateos et al. [67] developed a kinetic model for oxygen concentration dependence, creating a FORTRAN® program based on a Runge–Kutta algorithm to estimate the kinetic parameters for the hydrothermal oxidation of MeOH, besides acetic acid and phenol.

Portela et al. [1] applied the kinetics proposed by Mateos et al. [67] to simulate the SCWO process of highly concentrated feeds. This method was also used for the SCWO of cutting fluids by Sánchez-Oneto et al. [68] and, besides, the kinetic equation proposed in that work was applied by Jimenez-Espadafor et al. [7] in the simulation of the SCWO process with the aim of evaluating the viability of energy production by a SCWO industrial scale plant.

Hereafter we include a detailed explanation of how the Runge–Kutta method was conducted in this work to develop the kinetic model. Analogously to the above, Eq. (9) can be used to represent the transformation global rate of organic compounds to CO₂ and H₂O by means of SCWO:

$$r_{\text{COD}} = -\frac{d[\text{COD}]}{d\tau} = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot [\text{COD}]^\alpha \cdot [\text{O}_2]^\beta \cdot [\text{H}_2\text{O}]^\gamma \quad (9)$$

where [COD] is the total chemical oxygen demand (mol l⁻¹), *A* is the pre-exponential factor ((mol l⁻¹)^{1-α-β-γ} s⁻¹), *E_a* is the apparent activation energy (J mol⁻¹), *R* is the universal gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the temperature (K) and the reaction orders for organic matter, oxygen and water are α, β and γ, respectively. As previously shown through Eq. (3), Arrhenius temperature dependence is assumed for the specific reaction rate constant (*k*).

If also assumed that α = 1 and that γ = 0, Eq. (9) can be simplified as follows:

$$r_{\text{COD}} = -\frac{d[\text{COD}]}{d\tau} = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot [\text{COD}] \cdot [\text{O}_2]^\beta \quad (10)$$

According to Mateos et al. [67], the oxygen concentration at any time can be expressed as a function of the initial oxygen concentration and the reduction in COD concentration:

$$[\text{O}_2] = [\text{O}_2]_0 - ([\text{COD}]_0 - [\text{COD}]) \quad (11)$$

Therefore, the global rate for [COD] disappearance can be expressed as follows:

$$\begin{aligned} r_{\text{COD}} &= -\frac{d[\text{COD}]}{d\tau} \\ &= A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot [\text{COD}] \cdot ([\text{O}_2]_0 - ([\text{COD}]_0 - [\text{COD}]))^\beta \\ &= f(\tau, \text{COD}) \end{aligned} \quad (12)$$

where [COD]₀ and [O₂]₀ correspond to τ = 0. Eq. (12) was solved numerically using the Runge–Kutta method, determining the kinetic parameters (*k* and β) that produce the best fitting of experimental and calculated data. In this algorithm, the integration interval from 0 to the global residence time (τ_n) was divided into *n* subintervals with *h* = τ_n/*n*. This method is called “one step” because the determination of the function in the point *n* + 1 only requires the differential equation and information corresponding to the variables in the preceding point *n*. Specifically we used a Runge–Kutta-fourth order algorithm which, in this case, is expressed as in the following equation:

$$[\text{COD}]_{n+1} = [\text{COD}]_n + \frac{h}{6} \cdot (p_1 + 2p_2 + 2p_3 + p_4) \quad (13)$$

where *n* = 0, ..., *n* – 1 and:

$$p_1 = f(\tau_n, [\text{COD}]) \quad (14)$$

$$p_2 = f\left(\tau_n + \frac{h}{2}, [\text{COD}] + \frac{h}{2} \cdot p_1\right) \quad (15)$$

$$p_3 = f\left(\tau_n + \frac{h}{2}, [\text{COD}] + \frac{h}{2} \cdot p_2\right) \quad (16)$$

$$p_4 = f(\tau_n + h, [\text{COD}] + h \cdot p_3) \quad (17)$$

For the first run of the algorithm, the initial values of the kinetic parameters (*k* and β) are the ones issued from a previous study [68] where this method was applied for the SCWO of cutting fluids. Knowing the initial concentration at τ = 0 for COD and O₂, i.e. [COD]₀ and [O₂]₀, the application of Eqs. (12)–(17) allowed [COD]₁ to be determined for a residence time τ₁ = 1 · τ_n/*n*, i.e. for one subinterval (*h*). In the following run of the algorithm, using the calculated value for [COD]₁ it is possible to estimate [COD]₂ for τ₂ = 2 · τ_n/*n* (i.e. for two subintervals) and, similarly, successive runs allow the estimation of the different values of [COD] until obtaining the [COD]_{*n*} value for the global residence time τ_n. Finally, the estimated COD concentration values, [COD]_{*n-EST*}, were compared with the corresponding experimental COD concentration values, [COD]_{*n-EXP*}, and an adjustment of both *k* and β values was made in order to minimize the objective function presented as Eq. (18), which represents the difference between the estimated and experimental [COD] values:

$$\text{Objective function} = \sum_0^n ([\text{COD}]_{n-EST} - [\text{COD}]_{n-EXP})^2 \quad (18)$$

Based on Sánchez-Oneto et al. [68], developing of a Runge–Kutta algorithm and performing of the stated estimations were conducted through SOLVER[®] on MS EXCEL[®]. The kinetic parameters determination was performed according to the following procedure: first, using the results from the experiments carried out at 748 K and different oxidant coefficients (Table 5), the reaction order for oxygen (β) and the specific reaction rate constant corresponding to that temperature (*k*_{748 K}) were determined. Then, once the value of β was known, results from the experiments conducted under *n* = 2.0 at 673, 698, 723 and 773 K (Table 2) were used to define the value of the corresponding specific reaction rate constants: *k*_{673 K}, *k*_{698 K}, *k*_{723 K} and *k*_{773 K}. The results obtained for the kinetic parameters are presented in Table 6.

Once the specific reaction rate constant (*k*) is estimated for every studied temperature by fitting their values in an Arrhenius plot (Fig. 4), the values of the pre-exponential factor (*A* [(mgO₂ l⁻¹)^{-β} s⁻¹]) and the apparent activation energy (*E_a* [J mol⁻¹]) were obtained with a 95% confidence level.

Thereby, the SCWO of IPA global rate expression (Eq. (19)) for oxygen concentration dependence can be expressed as follows:

$$\begin{aligned} r_{\text{COD}} &= -\frac{d[\text{COD}]}{d\tau} \\ &= (158.8 \pm 57.7) \times 10^5 \cdot \exp\left(-\frac{(153.5 \pm 36.1) \times 10^3}{RT}\right) \\ &\quad \cdot [\text{COD}] \cdot [\text{O}_2]^{0.774} \end{aligned} \quad (19)$$

where the residence time (τ) is expressed in seconds (s), the temperature (*T*) in Kelvin (K), the universal gas constant *R* = 8.314 J mol⁻¹ K⁻¹, while COD and O₂ concentrations are expressed in mg l⁻¹.

Eq. (19) allows calculating the COD concentration of the effluent from the SCWO process and therefore the COD conversion (*X*_{COD}).

Table 6

Parameters of the kinetic model for oxygen concentration dependence considering the removal of COD in the SCWO of IPA, at 25 MPa.

Temperature (K)	<i>k</i> [(mgO ₂ l ⁻¹) ^{-β} s ⁻¹]	β
673	(1.63 ± 0.03) × 10 ⁻⁵	0.774 ± 0.023
698	(5.60 ± 0.11) × 10 ⁻⁵	
723	(1.54 ± 0.32) × 10 ⁻⁴	
748	(3.43 ± 0.66) × 10 ⁻⁴	
773	(5.43 ± 1.12) × 10 ⁻⁴	

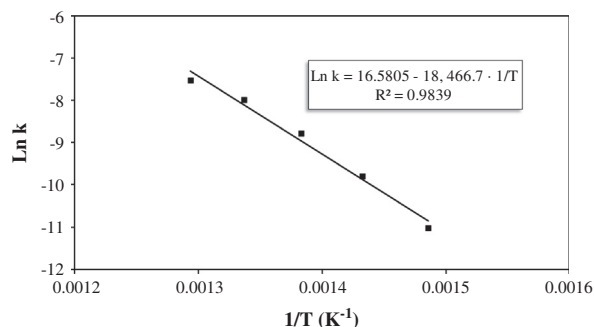


Fig. 4. Arrhenius plot for the specific reaction rate constant (k) values estimated by the Runge–Kutta algorithm (corresponding to the kinetic model for oxygen concentration dependence in the SCWO of IPA, at 25 MPa).

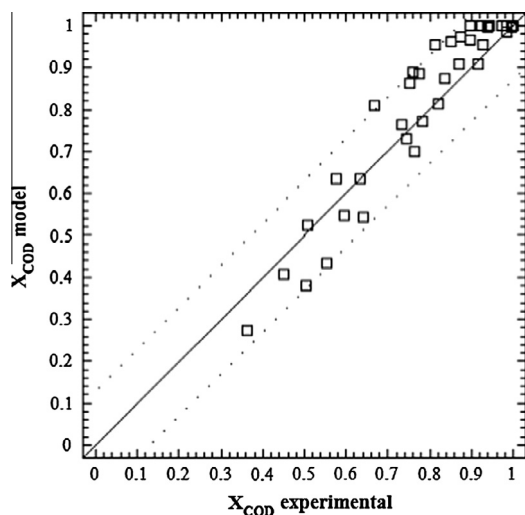


Fig. 5. Predicted conversions ($X_{\text{COD model}}$) versus Observed conversions ($X_{\text{COD experimental}}$) plot.

Eq. (20)) for the given operating conditions (including the employed oxygen excess).

$$X_{\text{COD}} = \frac{[\text{COD}]_0 - [\text{COD}]}{[\text{COD}]_0} \quad (20)$$

In Fig. 5 the conversions predicted by Eq. (19) are plotted versus the experimental ones obtained from the tests shown in Tables 2 and 5.

As it can be verified in Fig. 5, although data are a bit dispersed from the diagonal, this kinetic model embodies the general trend of experimental data for a reasonable $\pm 10\%$ confidence interval. It has to be taken into account that the kinetic model for oxygen concentration dependence is more efficient for the adjustment of data corresponding to the lowest residence times studied (fast reaction step) than for the adjustment of data corresponding to the highest residence times studied (slow reaction step). However, in general, it is able to predict the conversion enhancement when the oxidant coefficient (n) varies from oxygen deficiency to oxygen excess (that is not possible for the previous kinetic model that considered the oxygen supply always in excess).

4. Conclusions

The results shown in this work corroborate that isopropanol (IPA) is indeed a suitable fuel for supercritical water oxidation (SCWO) since, besides having an important heat of reaction, it

was easily oxidized in supercritical water (SCW) and was resistant to pyrolysis–hydrolysis.

A set of kinetic equations have been developed for the oxidation of IPA in SCW. On the one hand, two-parameter mathematical models involving two steps (a fast reaction followed by a slow reaction) were proposed, assuming a pseudo-first order kinetics since all experiments were carried out under oxygen excess. These models have a high predictive power if operating under oxygen excess conditions. It is applicable for further studies dealing with the use of IPA as auxiliary fuel in the start-up stage of the SCWO process.

On the other hand, a complementary kinetic model was developed using a Runge–Kutta algorithm, including the estimation of the reaction order for oxygen concentration. It is applicable for further studies that deal with the use of IPA as co-fuel in the SCWO process under steady state operation. However, care must be taken when applying this model, since the experimental results follow a clear two-step trend; it is able to predict the conversion enhancement when the oxidant coefficient (n) varies from oxygen deficiency to oxygen excess, being more efficient in the prediction of data corresponding to the fast reaction step than in the prediction of data corresponding to the slow reaction step. Therefore, in this field, it is recommended that the development of kinetic models based on Runge–Kutta algorithms and their applications are approached with caution.

The kinetic models proposed in this work allow the prediction of the COD or TOC conversion with or without respect to oxygen supply for the SCWO of IPA. This may aid the optimization of the operating conditions and the minimization of investment and operating costs in the SCWO of wastewaters/wastes with low inherent heating value, high acute toxicity and/or high concentration of ammonia (such as obsolete chemical weapons, manure sludge and sewage sludge). Kinetics developed in this work may also be useful to study SCWO of wet biomass wastes (such as sewage sludge) using semiconductor manufacturing cleaning waste (which has a high content of IPA) as auxiliary fuel and co-fuel.

Acknowledgments

The Authors gratefully acknowledge financial support from the NOVEDAR_Consolider Project (CSD2007-00055) funded by the Spanish Ministry of Education and Science and from the EPOS Project (P07-RNM-03276) financed by the Junta de Andalucía (Spain).

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